

## Covalent Organic Frameworks as Exceptional Hydrogen Storage Materials

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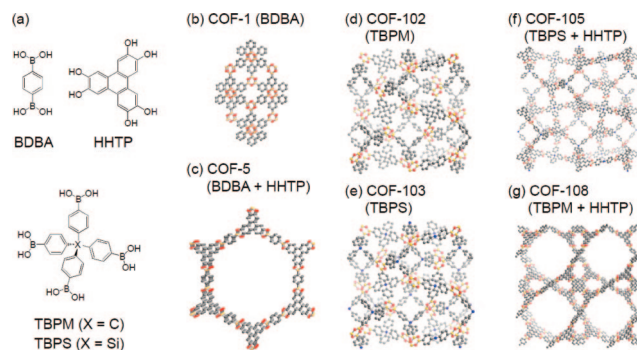
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Metal-organic frameworks (MOFs)<sup>1,2</sup> have emerged as promising hydrogen storage materials. The flexibility with which MOFs can be designed and their structural diversity have led to materials with ultrahigh porosity and exceptional H<sub>2</sub> uptake capacities.<sup>2a,b</sup> Recently, covalent organic frameworks (COFs) have been synthesized and structurally characterized.<sup>3</sup> Here the organic building units are held together by strong covalent bonds (C–C, C–O, B–O, and Si–C) rather than metal ions to produce materials with high porosity (3472 m<sup>2</sup>/g for COF-102 and 4210 m<sup>2</sup>/g for COF-103) and low crystal density (0.17 g/cm<sup>3</sup> for COF-108).<sup>3d</sup> These characteristics make COFs excellent candidates for storage of H<sub>2</sub>. Here, we report theoretical studies on prototypical COFs that predict up to 10% excess H<sub>2</sub> storage capacity in COF-105 at 77 K. We find excellent agreement with experimental H<sub>2</sub> loading data for COF-5, the one case for which we have been able to measure H<sub>2</sub> storage capacity under conditions in which we are confident to attain optimal activation (full evacuation of the pores). COF-1 and -5 are crystalline two-dimensional structures, while COF-102, -103, -105, and -108 have three-dimensional structures (Figure 1).<sup>3a,d</sup>

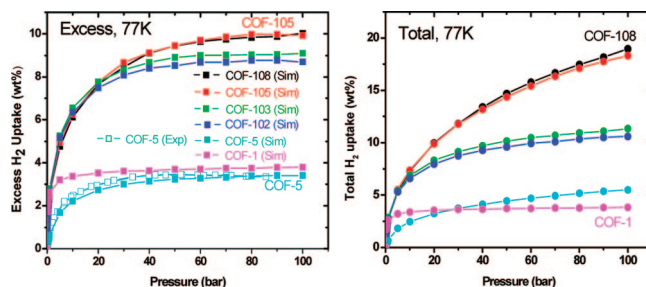
To predict the H<sub>2</sub> binding isotherm for these COFs as a function of temperature and pressure, we carried out grand canonical Monte Carlo (GCMC) simulations using the experimental COF structures from refs 3a and 3d. The force fields (FF) used in the GCMC simulation to describe the interactions between H<sub>2</sub> and COFs were derived from *ab initio* second-order Møller–Plesset (MP2) calculations using quadruple- $\zeta$  QZVPP basis set and basis set superposition error correction. These *ab initio* parameters are expected to be quite accurate [see Supporting Information (SI)].

Figure 2 shows the predicted H<sub>2</sub> uptake at 77 K, which are compared to experimental values for COF-5. Here the gravimetric excess is calculated as the total amount of gas contained in the pores minus the amount of gas that would be present in the pores in the absence of gas–solid intermolecular forces.<sup>4</sup> For COF-5 the theory (which was done prior to experiment) is in excellent agreement with experiment (3.3 vs 3.4 wt % at 50 bar), indicating that the theory can be used to identify the most promising materials for subsequent experiments. It is important to appreciate that meaningful comparison of theoretical and experimental results for COFs can only be done when measurements of H<sub>2</sub> uptake are done on samples known to have been optimally activated as we have confirmed for COF-5. Finding the right conditions for activation and complete removal of guests is a painstaking and time-consuming process. Because the theory predicts excellent performance for COF-105 and -108, we plan to focus such experiments on these systems.

We predict that the hydrogen storage capacity in the three-dimensional COFs (COF-102, -103, -105, and -108) is 2.5–3 times



**Figure 1.** Molecular structures of building units (a) and crystal structures of COFs (b–g). Hydrogen atoms are omitted for clarity. Carbon, boron, oxygen, and silicon atoms are represented as gray, orange, red, and blue spheres, respectively.



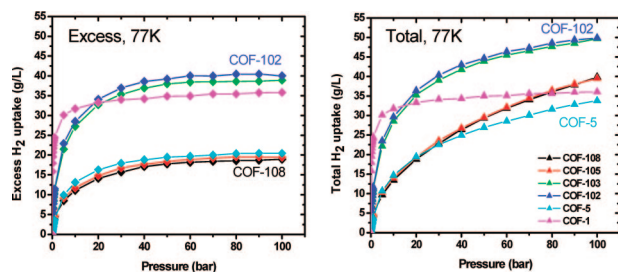
**Figure 2.** H<sub>2</sub> adsorption isotherms for COFs in gravimetric unit (wt %) at 77 K. Excess H<sub>2</sub> is on the left and total H<sub>2</sub> is on the right. Filled and open symbols represent simulation and experimental results, respectively.

higher than that in two-dimensional COFs (COF-1 and -5) because of higher surface area and free volume (see Table S2). The highest predicted excess H<sub>2</sub> uptakes at 77 K are 10.0 wt % at 80 bar for COF-105, and 10.0 wt % at 100 bar for COF-108. These values dramatically outperform representative MOFs whose H<sub>2</sub> uptakes (7.0 wt % for MOF-177<sup>1c</sup> and 7.1 wt % for MOF-5<sup>1j</sup>) were the highest measured. *Thus 3-D COFs are most promising new candidates in the quest for practical H<sub>2</sub> storage materials.*

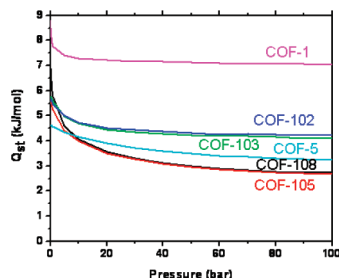
Specifically, we predict that COF-1 has a maximum H<sub>2</sub> uptake of 3.8 wt % at 70 bar, COF-5 has 3.4 wt % at 80 bar, COF-102 has 8.8 wt % at 80 bar, and COF-103 has 9.1 wt % at 100 bar, all at 77 K. For a pressure of 0.1 bar COF-1 shows the highest excess H<sub>2</sub> uptake (1.7 wt % of H<sub>2</sub> at 0.1 bar) which compares to 0.1 wt % for COF-5, 0.5 wt % for COF-102, 0.6 wt % for COF-103, 0.6 wt % for COF-105, and 0.9 wt % for COF-108 under the same conditions.

From the total adsorption isotherms at 77 K, we find COF-108 has the highest H<sub>2</sub> uptake primarily because of its highest free volume, with a maximum value of 18.9 wt % at 100 bar. This is followed by COF-105 (18.3 wt %), COF-103 (11.3 wt %), COF-

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**Figure 3.** Simulated  $\text{H}_2$  adsorption isotherms for COFs in volumetric units (g/L) at 77 K. Excess  $\text{H}_2$  is on the left and total  $\text{H}_2$  is on the right.



**Figure 4.** Calculated heats of adsorption ( $Q_{\text{st}}$ ) for  $\text{H}_2$  in COFs at 77 K.

102 (10.6 wt %), COF-5 (5.5 wt %), and COF-1 (3.8 wt %). The ratios of excess  $\text{H}_2$  uptake to total uptake at 100 bar is 0.99 for COF-1, by far the highest due to the smaller pore diameter. This ratio is 0.62 for COF-5, 0.82 for COF-102, 0.80 for COF-103, 0.54 for COF-105, and 0.52 for COF-108.

The volumetric  $\text{H}_2$  uptake isotherms for COFs are shown in Figure 3. Here, we predict that COF-1 is the best system up to a pressure of 20 bar, while COF-102 outperforms other COFs in the high pressure region. The maximum excess  $\text{H}_2$  uptake for COF-102 in volumetric units is 40.4 g/L at 100 bar, close to the 2010 DOE system goal of 45 g/L. [Other values at 100 bar are 35.8 g/L for COF-1, 20.5 g/L for COF-5, 38.9 g/L for COF-103, 19.4 g/L for COF-105, and 19.0 g/L for COF-108.] The 40.4 g/L of COF-102 is better than the 32.1 g/L of MOF-177,<sup>1c</sup> and 34.4 g/L for IRMOF-20,<sup>1c</sup> but slightly lower than the 43.4 g/L of MOF with exposed  $\text{Mn}^{2+}$  sites.<sup>11</sup> The maximum total  $\text{H}_2$  uptake in volumetric units is 36.1 g/L for COF-1, 33.8 g/L for COF-5, 49.9 g/L for COF-102, 49.8 g/L for COF-103, 39.5 g/L for COF-105, and 39.9 g/L for COF-108.

We also calculated isosteric heats of adsorption ( $Q_{\text{st}}$ )<sup>5</sup> for  $\text{H}_2$  at 77 K in various COFs (Figure 4) based on the total adsorbed amount of  $\text{H}_2$ . COF-1 has the highest  $Q_{\text{st}}$  at all pressures up to 100 bar with a maximum  $Q_{\text{st}} = 8.8$  kJ/mol, which is responsible for the high  $\text{H}_2$  storage at low pressure shown in Figures 2 and 3. The other maximum  $Q_{\text{st}}$  are 4.6 kJ/mol (COF-5), 5.7 kJ/mol (COF-102), 5.8 kJ/mol (COF-103), 5.6 kJ/mol (COF-105), and 7.4 kJ/mol (COF-108).

These calculations find that the most favored site for  $\text{H}_2$  adsorption at low pressure is on the benzene rings of the organic linkers, shown in Figure S2. This is consistent with the QM calculations, which lead to a binding of 3.81 kJ/mol for  $\text{H}_2$  to the benzene ring, 1.92 kJ/mol for bonding to boroxine, and 1.13 kJ/mol for silane.<sup>6</sup>

Our previous simulations<sup>2a</sup> for  $\text{H}_2$  adsorption sites in MOFs revealed that benzene rings on the organic linkers play an important role for  $\text{H}_2$  adsorption, particularly at increased hydrogen pressure, indicating that the organic linker is more important than the heavy transition metal element for the MOFs. The COFs have these benzene rings, but no transition metals.

After submission of this paper other reports of simulations<sup>7</sup> for gas uptake in COFs have appeared on line. These studies used empirical force fields, but, ref 7a found an  $\text{H}_2$  uptake of 10.5 wt % in COF-105 at 55 bar and 77 K, which compares well to the values we find of 9.4 wt % at 50 bar and 9.7 wt % at 60 bar (at 77 K) using our QM based FF.

Our GCMC simulations of COFs based on FF from accurate ab initio QM calculations predict  $\text{H}_2$  adsorption isotherms for COFs that agree well with the one known experimental case, validating the computational methodology. Using this theory, we predict that the best COF systems for hydrogen storage are COF-105 and COF-108, each of which lead to a maximum excess  $\text{H}_2$  uptakes of 10.0 wt % at 77 K. This is highest value reported for associative  $\text{H}_2$  storage of any material. In terms of total  $\text{H}_2$  uptake, the best is COF-102, with 18.9 wt % at 77 K. The best for volumetric uptake is COF-102, which can store 40.4 g/L of  $\text{H}_2$ . These results suggest COF systems as most promising materials for hydrogen storage. These results suggest that to further increase the maximum  $\text{H}_2$  uptake in COFs one should increase both their surface area and free volume. To obtain high  $\text{H}_2$  uptake at 300 K, we suggest doping with electropositive elements (such as Li, Na, K, and maybe Cu, Ag, and Au)<sup>2b</sup> to increase  $\text{H}_2$  binding energy.

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**Supporting Information Available:** Tables of the  $\text{H}_2$  adsorption (total and excess) isotherms for COFs at 77 K and  $\text{H}_2$  adsorption sites in COF-108 at 77 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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